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⑭発明の名称 密閉形アルカリ蓄電池

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明 細 書

1、発明の名称

密閉形アルカリ蓄電池

2、特許請求の範囲

(1) 式 $LaNi_xCo_yM_z$（但し、MはAl,Sn,Mg,Fe,Mo,Ta,V,Cr,Cu,Mn 及びNb よりなる群から選んだ少なくとも1種、$1.5 < x < 4.0$、$0 \leqq z \leqq 1$、$3 < x + y < 5.5$、$4 < x + y + z < 5.5$、で表わされる水素吸蔵合金からなる負極，正極，セパレータ及びアルカリ電解液を有する密閉形アルカリ蓄電池。

(2) 前記式において $x + y + z = 5$ である特許請求の範囲第1項記載の密閉形アルカリ蓄電池。

(3) 前記合金が、$LaNi_3Co_{1.7}Al_{0.3}$、$LaNi_{2.7}Co_{2.0}Al_{0.3}$ または $LaNi_3Co_2$ である特許請求の範囲第2項記載の密閉形アルカリ蓄電池。

3、発明の詳細な説明

産業上の利用分野

本発明は、電気化学的に水素を吸蔵，放出する水素吸蔵合金を負極に用いた 閉形アルカリ蓄電池に関する。

従来例の構成とその問題点

二次電池としては、鉛蓄電池，ニッケル－カドミウム蓄電池が最もよく知られているが、これらの蓄電池は負極の中に固形状の活物質を含むために、重量または容量の単位当りエネルギー貯蔵容量が比較的少ない。このエネルギー貯蔵容量を向上させるために、負極として水素吸蔵電極を用い、正極には例えばニッケル酸化物を用いた蓄電池が提案されている。負極には、LaNi 系やCa-Ni系などの水素吸蔵合金が用いられる。この電池系は、ニッケル－カドミウム蓄電池より高容量化が可能で、低公害の蓄電池として期待されている。

Ca-Ni系合金の代表的なものである $CaNi_5$ 合金を電極として用いた場合、安価で初期容量が大きいが、サイクル寿命が短い上に、放電電位が低いという欠点がある。

一方、La-Ni系合金の代表的なものである $LaNi_5$ 合金を負極として用いると、サイクル寿命は $CaNi_5$ 合金を用いたものと比べて良好であるが、

常温付近における放電容量が小さいという問題がある。さらに、密閉形蓄電池を構成した場合、初期の充放電サイクルでは過充電により電池内圧は上昇しないが、10サイクル程度の充放電により電池内圧は少しずつ上昇し放電容量も低下する。

また、$LaNi_5$ の改良として $La_{1-x}R_xNi_{5-y}M_y$ (ただし、RはCa,Thまたは希土類元素、MはCo,CuまたはFe、$0<x<1$、$0\leqq y\leqq 1$)が提案されている(特開昭61-45234)。この合金を用いると、比較的高い放電電圧と放電容量を示すが、密閉化した電池では過充電サイクルと共に電池内圧が上昇し、比較的サイクル寿命が短かくなるなどの問題点があった。

発明の目的

本発明は、上記従来の問題点を解消するもので、特に過充電により電池内圧の上昇が少ない密閉形アルカリ蓄電池を得ることを目的とする。

発明の構成

本発明の密閉形アルカリ蓄電池は、式 $LaNi_xCo_yM_z$ (式中、$1.5<x<4$、$0\leqq z\leqq 1$、$3<x+y<5.5$、$4<x+y+z<5.5$、MはAl,Sn,Mg,Fe,Mo,Ta,V,Cr,Cu,Mn及びNbよりなる群から選んだ少なくとも1種)で表わされる水素吸蔵合金を負極とし、セパレータを介して正極を配置し、アルカリ性電解液と共に密閉構造としたものである。

実施例の説明

市販のLa(純度99.5%以上)、Ni,Coの他に、前記式のMとしてAl,Sn,Mg,Fe,Mo,Ta,V,Cr,Cu,Mn,Nbなど少なくとも1種を選択し、各試料を一定の組成比に秤量,混合し、アーク溶解炉に入れて、$10^{-4}\sim10^{-5}$ Torr まで真空状態にした後、減圧状態のAr ガス雰囲気中でアーク放電し、加熱溶解させた。試料の均質化を図るために数回反転させて合金試料を得た。比較のために $LaNi_5$、$La_{0.9}Ca_{0.1}Ni_{4.5}Co_{0.5}$ 合金を用いた。これらの合金を粗粉砕後、ボールミルなどで38 μm以下の微粉末にした後、ポリエチレン7.5重量%と混合した。これらの混合粉末をアルコールと共にニッケル製発泡状金属多孔体内に充填し、乾燥後、1.8トン/cm²の圧力で加圧し、次に真空中120℃で熱処理し、リードを取り付け電極とした。

実施例で用いた電極の合金組成を表に示す。

各電極の合金量は約1.5gとし、公知の焼結式ニッケル正極と組合せて単2型の密閉形ニッケル一水素蓄電池(公称容量2.0Ah)を構成した。なお、正極律則となるよう、正極の容量を負極のそれより小さくした。

これらの電池を0.1Cで16時間充電し、0.2Cで放電する充放電を繰り返し、サイクル寿命と電池内圧を調べた。これらの結果を表に示す。

以 下 余 白

電極 No.	組 成 式	サイクル数 (〜)	充電末期の電池圧力 (kg/cm²)
1	$LaNi_5$	50	10以上
2	$La_{0.9}Ca_{0.1}Ni_{4.5}Co_{0.5}$	150以上	10以上
3	$LaNi_{2.7}Co_2Al_{0.3}$	200以上	2.3
4	$LaNi_3Co_{1.7}Al_{0.3}$	200以上	2.5
5	$LaNi_{3.5}CoAl_{0.5}$	200以上	4.8
6	$LaNi_3Co_2$	200以上	6.0
7	$LaNi_3Co_{1.7}Sn_{0.3}$	200以上	4.2
8	$LaNi_3Co_{1.7}Mg_{0.3}$	200以上	4.5
9	$LaNi_3Co_{1.7}Fe_{0.3}$	200以上	5.5
10	$LaNi_3Co_{1.7}Fe_{0.3}Mo_{0.1}$	200以上	4.9
11	$LaNi_3Co_{1.7}Ta_{0.3}V_{0.1}$	200以上	4.5
12	$LaNi_3Co_2Cr_{0.3}$	200以上	3.5
13	$LaNi_3Co_2Mn_{0.1}$	200以上	5.8
14	$LaNi_2Co_2Al_{1.2}$	150	8.0以上

1,2,4,~~6~~7, 12,16

1,12,16,6

Y5

表からわかるように、$LaNi_5$ 合金からなる電極1を用いた電池は充放電サイクル初期の電池内圧は3.5kg/cm² と低いが、50サイクルに達する

と、放電容量は著しく低下して初期容量の約½程度となり、過充電状態が厳しくなるため電池内圧も10kg/cm²以上にまで上昇する。

また、電極2を用いた電池は、充放電50サイクルまでは2.5kg/cm²の電池内圧を示し、初期は比較的良好な特性を示すが、充放電100サイクルを越えると電池内圧が急に上昇する傾向にある。150サイクルで10kg/cm²以上の電池内圧を示し、$LaNi_5$と同様に放電容量の低下が認められた。

これに対して、本発明の電極3〜13を用いた電池は充・放電を200サイクル継続しても放電容量の低下は比較的少なく、充電末期の電池内圧も2.5〜6.0kg/cm²程度である。電極14は、前記式におけるzが1より大きい合金を用いた例であり、サイクル寿命も短く、電池内圧も他の電池より高くなっている。したがって、zは1以下が優れている。z=0、すなわち$LaNi_3Co_2$などはサイクル寿命は長いがやゝ電池内圧が上昇する傾向にある。したがって金属Mは電池内圧上昇を抑制する効果がある。中でもAl は他の金属と比較して電池内圧の上昇を抑制する効果が大きい。Alについで、Cr,Ta,V,Mg,Sn,Mo,Mn なども比較的大きな効果が認められる。

また合金中のNi 原子が1原子以下であれば、Co 量が当然多くなり、電池の放電電圧の低下と共に一部Co の溶解現象が認められる。一方、Niの原子が4原子以上であればCo 量が少なくなり$LaNi_5$に近い特性となって、優れた密閉形アルカリ蓄電池とならない。したがって、xの値として、1.5<x<4の範囲が最適である。また金属Mとしては、水素平衡圧力を下げる働きをする金属が望ましい。

本発明による水素吸蔵電極を用いた電池は、正極から発生する酸素ガスが負極の表面で負極中に含有する水素と電気化学的に反応して水にかえす過程をくりかえすために、内圧の上昇が少ない。しかも負極の表面では優先的に水素と酸素のみが作用するしくみになっている。そして酸素に対して腐食されない耐久性のある合金負極を与えている。合金中のNi は1.5原子から4原子までにして、Co を1原子以上にすることが好ましい。さらに、Mは1原子以下とし、$LaNi_xCo_yM_z$において、4<x+y+z<5.5の範囲内が優れている。なかでもx+y+z=5の合金組成で、とくに$LaNi_3Co_{1.7}Al_{0.3}$,$LaNi_{2.7}Co_{2.0}Al_{0.3}$などが優れている。$LaNi_xCo_y$合金では$LaNi_3Co_2$が比較的優れた特性を示している。

合金中のNi 原子を減少させることにより、水素の吸蔵性能を、またCo 原子を増加させることによりサイクル寿命の向上と内圧上昇の抑制を図り、さらに金属Mなどで耐久性を増加し、電池全体としての性能を著しく向上させることができる。

発明の効果

以上のように、本発明によれば、充放電のサイクル寿命に優れ、過充電により電池内圧の上昇が少ない信頼性の高い密閉形アルカリ蓄電池が得られる。

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Japanes Patent Provisional Publication No. 60-250557/1985

Specification

1. TITLE OF THE INVENTION

Sealed Alkaline Battery

2. WHAT IS CLAIMED IS:

(1) A sealed alkaline battery comprising a negative electrode, comprising a hydrogen storage alloy expressed by the formula $LaNi_xCo_yM_z$ (where M is at least one element selected from the group consisting of Al, Sn, Mg, Fe, Mo, Ta, V, Cr, Cu, Mn, and Nb, $1.5 < x < 4.0$, $0 \leqq z \leqq 1$, $3 < x + y < 5.5$, and $4 < x + y + z < 5.5$); a positive electrode; a separator; and an alkaline electrolyte.

(2) The sealed alkaline battery according to Claim 1, wherein $x + y + z = 5$ in said formula.

(3) The sealed alkaline battery according to Claim 2, wherein said alloy is expressed by $LaNi_3Co_{1.7}Al_{0.3}$, $LaNi_{2.7}Co_{2.0}Al_{0.3}$ or $LaNi_3Co_2$.

3. DETAILED DESCRIPTION OF THE INVENTION

Field of the Industrial Application

This invention relates to a sealed alkaline battery comprising a negative electrode of a hydrogen storage alloy,

which stores and releases hydrogen electrochemically.

Prior Art and Problems Thereof

Although a lead battery and a nickel-cadmium battery are the most well-known types of secondary batteries, since these batteries contain a solid active substance in the negative electrode, they are comparatively low in the energy storage capacity per unit weight or volume. A battery comprising a hydrogen storage electrode as the negative electrode and, for example, a nickel oxide as the positive electrode, has been proposed for improving the energy storage capacity. A hydrogen storage alloy such as an LaNi alloy and Ca-Ni alloy is used as the negative electrode. This battery system can realize higher capacity than nickel-cadmium batteries and is expected as a low-pollution battery.

When the $CaNi_5$ alloy, a typical example of the Ca-Ni alloy, is used in an electrode, the cost is low and the initial capacity is high. However, there are the disadvantages of short cycle life and low discharge voltage.

On the other hand, when the $LaNi_5$ alloy, a typical example of the La-Ni alloy, is used, the cycle life therefor is better than that for the $CaNi_5$ alloy. However, there is the problem of low discharge capacity around room temperature. Furthermore, when a sealed battery is formed, the internal battery pressure is not raised by overcharging in the initial

charge/discharge cycle, but is raised gradually on or after about the 10th charge/discharge cycle with the discharge capacity also dropping.

As an improved replacement for $LaNi_5$, $La_{1-x}R_xNi_{5-y}M_y$ (where R is Ca, Th, or a rare earth metal, M is Co, Cu, or Fe, $0 < x < 1$, and $0 \leqq y \leqq 1$) has been proposed (Japanese Patent Provisional Publication No. 51-45234/1976). When this alloy is used, a comparatively high discharge voltage and discharge capacity are exhibited. However, a sealed battery has problems that the internal battery pressure rises and the cycle life becomes relatively short by the overcharging cycle.

Purpose of the Invention

The purpose of this invention is to resolve the above problems for the prior art and to provide a sealed alkaline battery having a lowered increase of the internal battery pressure by overcharging.

Construction of the Invention

According to this invention, a sealed alkaline battery comprises a negative electrode of a hydrogen storage alloy expressed by the formula

$LaNi_xCo_yM_z$

wherein

$1.5 < x < 4$, $0 \leqq z \leqq 1$, $3 < x + y < 5.5$, $4 < x + y + z$

< 5.5, and M is at least one element selected from the group consisting of Al, Sn, Mg, Fe, Mo, Ta, V, Cr, Cu, Mn, and Nb,

and a positive electrode disposed across a separator, these components being arranged in a sealed structure along with an alkaline electrolyte.

Examples of the Preferred Embodiments

In addition to commercially available La (of a purity of 99.5% or more), Ni and Co, at least one element was selected from the group consisting of Al, Sn, Mg, Fe, Mo, Ta, V, Cr, Cu, Mn, and Nb as M in the above formula. The respective samples were weighed and mixed to predetermined composition ratios and placed in an arc melting furnace. After the evacuation to 10^{-4} to 10^{-5} Torr, arc discharge was performed under a reduced pressure of Ar gas atmosphere to heat and melt the samples. The samples were made uniform by rotating them a few times so as to yield alloy samples. $LaNi_5$ and $La_{0.9}Ca_{0.1}Ni_{4.5}Co_{0.5}$ alloys were used for comparison. After each of these alloys was coarsely pulverized, it was pulverized into a fine powder of 38µm or less by a ball mill, etc. It was mixed with 7.5% by weight of polyethylene. Each of these mixed powders was filled along with alcohol in foamed metal porous bodies of nickel, and after being dried, compressed at a pressure of 1.8 ton/cm², heat treated at

120°C in vacuum, and made into an electrode by attachment of a lead.

The alloy compositions for electrodes used in the examples are shown in the Table.

Having approximately 15g of alloy in each electrode, a size AA sealed nickel-hydrogen storage battery (nominal capacity: 2.0Ah) was formed by combining with a known sintered nickel positive electrode. In order to make the battery positive electrode governing, the capacity of the positive electrode was made smaller than that of the negative electrode.

These batteries were charged for 16 hours at 0.1C and subject to repeated charging/discharging in which charging at 0.2C was performed to evaluate the cycle life and internal battery pressure. The results are shown in the Table.

Electrode No.	Composition formula	Number of cycles (∞)	Battery pressure at the firal stage of charging (kg/cm^2)
1	$LaNi_5$	50	10 or more
2	$La_{09}Ca_{0.1}Ni_{4.5}Co_{0.5}$	150 or more	10 or more
3	$LaNi_{2.7}Co_2Al_{0.3}$	200 or more	2.3
4	$LaNi_3Co_{1.7}Al_{0.3}$	200 or more	2.5
5	$LaNi_{3.5}CoAl_{0.5}$	200 or more	4.8
6	$LaNi_3Co_2$	200 or more	6.0
7	$LaNi_3Co_{1.7}Sn_{0.3}$	200 or more	4.2
8	$LaNi_3Co_{1.7}Mg_{0.3}$	200 or more	4.5
9	$LaNi_3Co_{1.7}Fe_{0.3}$	200 or more	5.5
10	$LaNi_3Co_{1.7}Fe_{0.3}Mo_{0.1}$	200 or more	4.9
11	$LaNi_3Co_{1.7}Ta_{0.3}V_{0.1}$	200 or more	4.5
12	$LaNi_3Co_2Cr_{0.3}$	200 or more	3.5
13	$LaNi_3Co_2Mn_{0.1}$	200 or more	5.8
14	$LaNi_2Co_2Al_{1.2}$	150	9.0 or more

As can be understood from the Table, according to a battery with an electrode 1 comprising a $LaNi_5$ alloy, the internal battery pressure at the beginning of the charge/discharge cycle takes on low value of $3.5kg/cm^2$. When 50 cycles are reached, however, the discharge capacity drops significantly and becomes approximately one third the initial capacity and the internal battery pressure rises to $10kg/cm^2$ or more by the severe overcharging.

According to a battery with electrode 2, although an internal battery pressure of $2.5kg/cm^2$ is exhibited up to 50

cycles of charging/discharging and comparatively good characteristics are exhibited initially, the internal battery pressure tends to rise rapidly beyond 100 cycles of charging/discharging. At 150 cycles, the internal battery pressure became 10kg/cm^2 or more and the discharge capacity was lowered in the same manner of $LaNi_5$.

On the other hand, according to batteries of this invention with electrodes 3 to 13, reduction of the discharge capacity is comparatively low even when 200 cycles of charging/discharging have been continued and the internal battery pressure at the final stage of charging is only approximately 2.5 to 6.0 kg/cm^2. Electrode 14 is an example in which the alloy keeping z in the above formula greater than 1 is used. According to Electrode 14, the cycle life is short and the internal battery pressure is also higher than those of the other batteries. Thus, z being 1 or less excels. When z = 0, that is, in the case of $LaNi_3Co_2$, etc., though the cycle life is long, there is a tendency for the internal battery pressure to rise somewhat. Thus, the metal M has the effect of restraining the rise of the internal battery pressure. Among the metals M, Al has higher effect of restraining the rise of the internal battery pressure than the other metals. After Al, comparatively high effects are also seen with Cr, Ta, V, Mg, Sn, Mo, Mn, etc.

Also, when there is 1 or less atoms of Ni in the alloy,

the amount of Co obviously increases, exhibiting the lowering of the discharge voltage of the battery as well as the partial dissolution of Co. On the other hand, when there are 4 or more atoms of Ni, the amount of Co decreases, exhibiting the similar properties to those of $LaNi_5$. Thus, an excellent sealed alkaline battery is not provided. Hence, in regard to the value of x, the range of $1.5 < x < 4$ is optimal. As the metal M, a metal that functions to lower the hydrogen equilibrium pressure is preferable.

According to the battery of this invention which uses a hydrogen storage electrode, the process in which the oxygen gas generated from the positive electrode reacts electrochemically with the hydrogen contained in the negative electrode at the surface of the negative electrode so as to yield water, is repeated. Thus, the rise of internal pressure is low. Moreover, it is designed so that only hydrogen and oxygen react with priority at the surface of the negative electrode. A durable alloy negative electrode which is not corroded by oxygen is also provided. The amount of Ni in the alloy is preferably set from 1.5 atoms to 4 atoms and the amount of Co is preferably set to 1 atom or more. Furthermore, the amount of M is set to 1 atom or less, and $LaNi_xCo_yM_z$ having the range of $4 < x + y + z < 5.5$ is excellent. In particular, an alloy composition having $x + y + z = 5$ and especially, $LaNi_3Co_{1.7}Al_{0.3}$, $LaNi_{2.7}Co_{2.0}Al_{0.3}$, etc.

are excellent. In regard to an $LaNi_xCo_y$ alloy, $LaNi_3Co_2$ exhibits comparatively excellent properties.

By decreasing the amount of Ni atoms in the alloy, the hydrogen storage performance can be improved. By increasing the amount of Co atoms in the alloy, the cycle life can be improved and the rise of internal pressure can be restrained. By the presence of metal M and others, the durability can be increased significantly. Thus, the performance of the battery can be enhanced as a whole.

Effect of the Invention

As has been described above, according to this invention, a highly reliable sealed alkaline battery, being excellent in charging/discharging cycle life and low in the rise of internal battery pressure by overcharging, can be provided.

Name of Representative: Toshio Nakao, patent attorney, and 1 other.

PTO 03-3696

Japanese Kokai Patent Application
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SEALED ALKALINE STORAGE BATTERIES

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SEALED ALKALINE STORAGE BATTERIES

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Claim

1. The sealed alkaline storage batteries contain a negative electrode made of hydrogen-occluding alloys which can be represented by the formula $LaNi_xCo_yM_z$ (wherein M is at least one metal selected from the group consisting of Al, Sn, Mg, Fe, Mo, Ta, V, Cr, Cu, Mn, and Nb, $1.5 < x < 4.0$, $0 \leq z \leq 1$, $3 < x + y < 5.5$, and $4 < x + y + z < 5.5$), a positive electrode, a separator, and an alkaline electrolytic solution.

2. In the sealed alkaline storage batteries described in Claim 1, $x + y + z = 5$ in the above-mentioned formula.

3. In the sealed alkaline storage batteries described in Claim 2, the above-mentioned alloys include $LaNi_3Co_{1.7}Al_{0.3}$, $LaNi_{2.7}Co_{2.0}Al_{0.3}$, or $LaNi_3Co_2$.

Detailed explanation of the invention

The present invention pertains to sealed alkaline storage batteries containing hydrogen-occluding alloys as negative electrodes which can electrochemically occlude and release hydrogen.

Constitution of conventional sealed alkaline storage batteries and their problems

Lead storage batteries and nickel-cadmium storage batteries are the most well-known secondary batteries. However, in these storage batteries the negative electrodes contain solid active materials, therefore the energy storage capacity per unit weight or volume is relatively small. Storage batteries were proposed which used hydrogen-occluding electrodes as the negative electrodes for improving the energy storage capacity and positive electrodes made of, for example, nickel oxides, and for the negative electrodes, LaNi and Ca-Ni alloys are used. The energy storage capacity of these batteries can have higher capacity than nickel-cadmium storage

batteries, therefore they are expected to be storage batteries with less environmental pollution than nickel-cadmium storage batteries.

When $CaNi_5$ alloy, which is a representative of Ca-Ni alloys, is used as an electrode, it is inexpensive and its initial capacity is large, however, there are drawbacks which include a short cycle life and low discharge electric potential.

On the other hand, when $LaNi_5$ alloy, which is a representative of La-Ni alloys, is used as a negative electrode, the cycle life is better than when $CaNi_5$ alloy is used, however, there is a problem of small discharge capacity in the vicinity of room temperature. Furthermore when a sealed storage battery is constituted, in the initial-stage discharge-charge cycle, the internal pressure of the battery does not rise by overcharging, but by approximately 10 discharge-charge cycles the internal pressure of the battery rises slowly and the discharge capacity drops also.

And for the improvement of $LaNi_5$, the use of $La_{1-x}R_xNi_{5-y}M_y$ (wherein R is Ca, Th, or a rare earth element, M is Co, Cu or Fe, $0 < x < 1.$ $0 \leq y \leq 1$) was proposed (Japanese Kokai Patent No.: Sho 51[1976]-45234). When this alloy was used, relatively high discharge electric potential and discharge capacity can be exhibited, however, in a sealed battery both the overcharge cycle and the internal pressure of the battery rise and the cycle life is relatively shortened, which are problems.

Object of the invention

The object of the present invention to eliminate the above-mentioned conventional problems and especially to obtain sealed alkaline storage batteries in which the rise of internal pressure due to overcharge is small.

Constitution of the invention

The sealed alkaline storage batteries of the present invention use hydrogen-occluding alloys which can be represented by the formula $LaNi_xCo_yM_z$ (wherein $1.5 < x < 4.0$, $0 \leq z \leq 1$, $3 < x + y < 5.5$, and $4 < x + y + z < 5.5$, M is at least one metal selected from the group consisting of Al, Sn, Mg, Fe, Mo, Ta, V, Cr, Cu, Mn, and Nb) as a negative electrode, a positive electrode, a separator between the negative electrode and the positive electrode, and an alkaline electrolytic solution.

Explanation of application examples

In addition to La (at least 99.5 % pure), Ni, and Co which were sold on the market, at least one metal selected from the group consisting of Al, Sn, Mg, Fe, Mo, Ta, V, Cr, Cu, Mn, and Nb was used, and each of the metal samples was weighed to have a specified composition, then they were mixed and put in an arc melting furnace, the inside of the furnace was evacuated to a

vacuum of 10^{-4} - 10^{-5} torr, then arc discharge was carried out in a reduced-pressure Ar gas atmosphere to dissolve them by heating. To obtain a homogeneous sample, the mixture of the metals was inverted several times to obtain an alloy sample. For comparison, $LaNi_5$ and $La_{0.9}Ca_{0.1}Ni_{4.5}Co_{0.5}$ alloys were used. After these alloys were coarsely pulverized, they were ground to fine powder by a ball mill to a particle size 38 μm or less, then they were mixed with 7.5 % by weight of polyethylene. These mixed powders and alcohol were filled in a foamed porous nickel and after drying, it was compressed with a pressure of 1.8 tons/cm^3, then heated at 120°C in vacuo, then a lead was mounted to create an electrode.

The composition of alloys which were used as electrodes in Application Examples is shown in the following table.

The alloy content of each electrode was approximately 15 g, and by combination with a well-known sintered nickel positive electrode, a sealed nickel-hydrogen storage battery (nominal capacity 2.0 Ah) was obtained. The capacity of the positive electrode was made smaller than that of the negative electrode.

These batteries were charged at 0.1 C for 16 hours, and discharge and charge to 0.26 was repeated to investigate the cycle life and the internal pressure of the batteries. The results are shown in the following table.

① 電極No.	② 組成式	③ サイクル数(回)	④ 充電末期の電池圧力 (kg/cm^2)
1	$LaNi_5$	60	10以上
2	$La_{0.9}Ca_{0.1}Ni_{4.5}Co_{0.5}$	150以上	10以上
3	$LaNi_{2.7}Co_{2}Al_{0.3}$	200以上	28
4	$LaNi_3Co_{1.7}Al_{0.3}$	200以上	26
5	$LaNi_{3.5}CoAl_{0.5}$	200以上	48
6	$LaNi_3Co_2$	200以上	20
7	$LaNi_3Co_{1.7}B_{0.3}$	200以上	42
8	$LaNi_3Co_{1.7}Mn_{0.3}$	200以上	48
9	$LaNi_3Co_{1.7}Fe_{0.3}$	200以上	66
10	$LaNi_3Co_{1.7}Fe_{0.2}Mn_{0.1}$	200以上	48
11	$LaNi_3Co_{1.7}Ti_{0.2}V_{0.1}$	200以上	46
12	$LaNi_3Co_2Cr_{0.3}$	200以上	36
13	$LaNi_3Co_2Mn_{0.1}$	200以上	58
14	$LaNi_3Co_2Al_{1.2}$	160	20以上 ⑤

Key: 1 Electrode No.
2 Composition formula
3 Cycle number
4 Battery pressure at the last stage of charging
5 Or greater

From the table it is clear that for the battery using the electrode 1 made of $LaNi_5$, the internal pressure of the battery at the initial stage of the discharge-charge cycle is as low as 3.6 kg/cm^2, however, when it reaches 50 cycles, the discharge capacity drops significantly to approximately 1/3 of the initial-stage capacity, and because the overcharge state becomes severe the internal pressure of the battery rises to 10 kg/cm^2 or greater.

And for the battery using the electrode 2, at up to 50 discharge-charge cycles 2.5 kg/cm^2 internal pressure of the battery is exhibited, and relatively good characteristics are exhibited at the initial stage, however, when it exceeds 100 discharge-charge cycles, there is a tendency of rapid rise of the internal pressure of the battery, and at 150 cycles 10 kg/cm^2 or greater internal pressure of the battery is exhibited, and like $LaNi_5$, a drop of discharge capacity is observed.

Contrary to this, for the batteries using the electrodes 1-3 of the present invention, even if 200 discharge-charge cycles were continuously carried out, the drop of discharge capacity was relatively small and the internal pressure of the batteries at the last stage of the charging was approximately 2.5-6.0 kg/cm^2. In the electrode 14, which is an example of using an alloy in which z is greater than 1 in the aforementioned formula, the cycle life is short and the internal pressure of the battery is higher than that of other batteries. Accordingly those alloys where z is 1 or less are excellent. When $z = 0$, that is, $LaNi_3Co_2$, etc., the cycle life is long but there is a tendency toward a slight rising of the internal pressure of the batteries. Thus metal M has the effect of suppressing the rise of the internal pressure of the batteries. Above all, the effect of Al in suppressing the rise of the internal pressure of the batteries is greater than other metals. Next to Al, the effect of suppressing the rise of the internal pressure of the batteries by Cr, Ta, V, Mg, Sn, Mo, Mn, etc. is also relatively large.

When the number of nickel atom in the alloy is one atom or less, the amount of Co of course becomes large, and with the drop of discharge electric potential of the battery, the dissolution of some of the Co can be observed. On the other hand when the number of nickel atoms in the alloy is 4 atoms or greater, the amount of Co becomes small and close to the characteristics of $LaNi_5$, thus an excellent sealed alkaline storage battery cannot be obtained. Accordingly the optimum value of x is in the range of $1.5 < x < 4$. For the metal M, those metals which can reduce the hydrogen equilibrium pressure are preferable.

In the batteries which use the hydrogen-occluding electrodes of the present invention, the oxygen gas generated at the positive electrode reacts electrochemically with the hydrogen gas in the negative electrode on the surface of the negative electrode to form water and the process is repeated, thus the increase of the internal pressure of the batteries is small. Moreover on the surface of the negative electrode, the hydrogen preferentially reacts with oxygen only. And durable alloy negative electrodes which are not corroded by oxygen are used. It is preferable to control the number of Ni atoms to 1.5 to 4 atoms and the number of Co atoms to one atom or

greater in the alloys. Furthermore M is controlled to one atom or less and for $LaNi_xCo_yM_z$, $4 < x + y + z < 5$ is excellent. Above all, in alloy compositions with $x + y + z = 5$, especially $LaNi_3Co_{1.7}Al_{0.3}$, $LaNi_{2.7}Co_{2.0}Al_{0.3}$ etc., are excellent. Among $LaNi_xCo_y$ alloys, $LaNi_3Co_2$ exhibits relatively excellent characteristics.

By reducing the number of Ni atoms in the alloys for improving the hydrogen-occluding property and by increasing the number of Co atoms in the alloys the cycle life of the batteries can be improved, and the rising of the internal pressure of the batteries can be suppressed, and furthermore the durability of the batteries can be improved by the use of the metal M, thereby the overall performance of the batteries can be improved remarkably.

Effect of the invention

As mentioned above, according to the present invention, reliable sealed alkaline storage batteries with an excellent charge-discharge cycle and minimal rise of the internal pressure of the batteries can be obtained.